Kinetic Aspects on Solid-State Transformations under High Pressure (Commemoration Issue Dedicated to Professor Eiji Suito on the Occasion of his Retirement)

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Review

Kinetic Aspects on Solid-State Transformations under High Pressure

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INTRODUCTION

Researches on solids under pressure, such as pressure-temperature relations of transitions, crystal structures, electronic structures, and other physical properties, have been eagerly performed by many physicists and geophysicists. The thermodynamic and atomic informations, however, are not enough to elucidate the mechanisms of chemical transformations. Chemists have a strong interest in what kind of atoms or molecules can combine and how they can change. The kinetic approach to transformations gives important informations which reveal the mechanism.

Papers concerning the kinetic approach to solid-state reactions, however, are relatively small in number, because of the difficulty in experimental techniques at high pressures and of the complexity in the factors controlling reactions due to the restriction of atomic migration in solids.

In our laboratory, the combination reactions between two kinds of elements have been studied for more than ten years. Table I lists the names of elements studied and the products at 1 atm as well as at high pressures together with their experimental conditions where the reactions occur in a measurable rate. High pressures up to 70 kb in ordinary use were generated in a compact cubic anvil apparatus[1] constructed in our laboratory in 1963. Table I includes also the substances cited from references. Although it seems difficult to deduce a general rule in the reactivity of elements, we can see only from Table I that the reactions between elements with small difference in ionization potentials and/or in atomic radii occur easily even at relatively low temperatures.

In this article, we will report especially two topics among the researches carried out in our laboratory, *i.e.* "the kinetics of polymorphic transitions in cadmium chalcogenides" and "the kinetics of solid-state reactions between two kinds of elements; Zn-P and Zn-As."

KINETICS OF POLYMORPHIC TRANSITIONS IN CADMIUM CHALCOGENIDES

At atmospheric pressure, the structure of CdS and CdSe is wurtzite type and that of CdTe is zinc blende type. It has been shown by volume change[24~26], electrical resistance

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Table I Examples of Inorganic Reactions at High Temperature and High Pressure

System		Atmospheric phase Product	Structure	High pressure phase Product	Structure	Condition of formation Temperature (°C)	Pressure (kb)	Reference
III–V	B–N	BN	hex	BN	cub-ZnS	1,700∼2,200	60∼90	2, 3
				BN	hex-ZnO	room temp.	140	4
	B–P	BP	cub-ZnS	BP	cub-ZnS	1,000∼1,400	5∼15	5
		$B_{13}P_2$	rhomb					
	B–As	BAs	cub-ZnS	BAs	cub-ZnS	800∼1,100	5∼40	6
		$B_{13}As_2$	rhomb	$B_{13}As_2$	rhomb	1,200∼1,400	5∼40	
IV–IV	Si–C	α-SiC	hex	β-SiC	cub-ZnS	700∼1,400	10∼50	7
		β-SiC	cub-ZnS					
IV–V	Si–P	SiP		SiP	cub-ZnS	1,400∼1,500	40∼50	8
		SiP_2	ortho	SiP_2	cub-FeS_2	1,000∼1,400	3∼40	
	Si–As	SiAs	mon	$SiAs_2$	cub-FeS_2	1,100∼1,300	45∼55	9
		$SiAs_2$	ortho					
	Ge–P	GeP	mon	GeP	cub-ZnS	1,400	40	10
				GeP	disordered-ZnS	1,350	40	
				GeP_2	cub-ZnS	1,000∼1,200	30∼40	
	Sn–P	SnP	hex	SnP	cub-ZnS	1,700	40∼50	
II–V	Zn–P	ZnP_2	mon	ZnP_2	mon	300∼600	5∼15	11
		ZnP_2	tet	ZnP_2	tet	600∼1,000	5∼20	
				ZnP_2	pseudo-cub	150∼	15∼	
		Zn_3P_2	tet	Zn_3P_2	tet	150∼400	5∼50	12
	Zn–As	Zn_3As_2	tet	Zn_3As_2	tet	150∼400	20∼40	13
III–VI	In–Te	InTe	tet	InTe	cub-NaCl	400∼500	30	14
	B–O	B_2O_3	hex	B_2O_3	mon	400∼700	22∼30	15
				B_2O	hex	1,200∼1,800	50∼75	16
				B_2O	cub	1,200∼1,800	120	
IV–VI	Si–S	SiS_2	ortho	SiS_2	tet	700∼1,500	50∼75	17, 18
	Ge–S	GeS	ortho	GeS_2	tet	1,100	45	
		GeS_2	ortho					
V–VI	Bi–S	Bi_2S_3	ortho	BiS_2	?	1,250	50	19
	Bi–Se	BiSe	cub-NaCl	$BiSe_2$	?	1,300	45	20
		$BiSe_2$	rhomb	BiSSe	?			
I–VI	Cu–S	CuS	hex	CuS_2	cub-FeS_2			21, 22
	Cu–Se	CuSe	hex	$CuSe_2$	cub-FeS_2	400∼	30	
	Cu–Te	CuTe	ortho	$CuTe_2$	cub-FeS_2			
II–VI	Zn, Cd – S, Se, Te	ZnS	cub-ZnS	ZnS_2	cub-FeS_2	800∼1,200	65	
		(AB)	hex-ZnO	(AB_2)				
VIII–V	Fe, Co, Ni – P, As	NiAs	hex	$NiAs_2$	cub-FeS_2	1,400	60	22, 23
		FeP	ortho	FeP_2	cub-FeS_2			
		(AB)		(AB_2)				
VIII–VI	Ir–S	IrS_2	ortho	IrS_2	cub-FeS_2	1,500	60	23

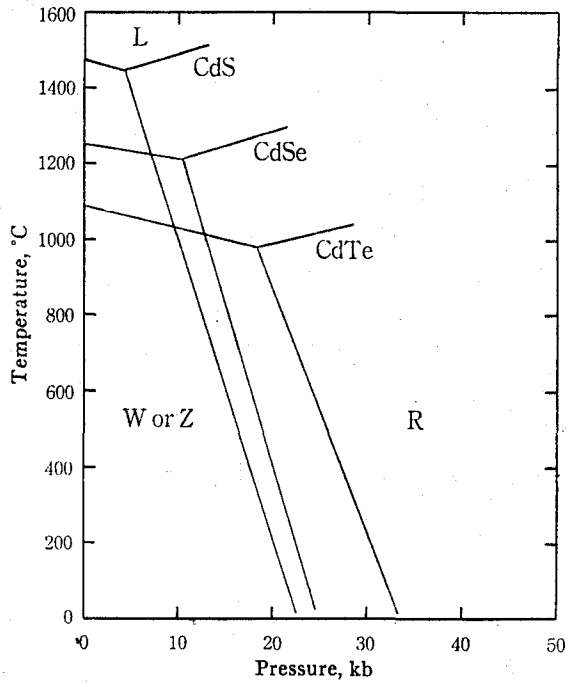

Fig. 1 Phase diagrams of cadmium chalcogenides.

[26~29], X-ray diffraction[30~35], and optical absorption measurements[36,37] that cadmium chalcogenides (CdS, CdSe, CdTe) undergo phase transitions to the cubic rock salt type structure under pressures of 20–40 kb. All of the low pressure phases of cadmium chalcogenides, which are semiconductors resistivities of $\sim 10^6$ Ωcm, transform to the high pressure phases accompanying with the decrease in resistivity of several orders. Thus, by measuring the electrical resistance, the phase boundaries of their transitions were determined first.[38~40] Figure 1 shows their phase diagrams.

The melting line of CdTe in Fig. 1 is from the data of Jayaraman *et al.*[24] While in CdS and CdSe, the melting lines are drawn on the assumption that the slopes of the melting curves may be similar to that of CdTe according to the suggestion that the entropy change and the volume change upon melting are constant for the crystals with similar structure.[41] The boundaries between low- and high- pressure phases cross the melting lines with the resulting triple points and the boundaries have negative slopes, which are

Table II Thermodynamic Parameters at the Transitions

Substance	Low pressure phase	High pressure phase	$10^2 \times dP/dT$ (kb/deg)	ΔV (cm^3/mol)	ΔS (e.u.)	$10^{-2} \times \Delta H$ (cal/mol)	Reference
CdS	Wurtzite	Rock salt	−1.3	−6.1	1.9	5.6	38
CdSe	Wurtzite	Rock salt	−1.2	−6.2	1.7	5.0	39
CdTe	Zinc blende	Rock salt	−1.5	−6.3	2.3	6.6	40
Ge	Diamond	White tin	−3.0	—	—	—	42
InSb	Zinc blende	White tin	−1.7	−3.9	1.7	5.0	43

compared with those of Ge and InSb. Table II gives the thermodynamic parameters at the transitions obtained from the Clapeyron equation, which also includes those of Ge and InSb.

The rates for the above mentioned solid phase transitions were obtained also by the measurement of electrical resistance.[44] The second-order rate equation was found to hold for all the measured data over the entire range of pressure and temperature studied.

$$\frac{1}{1-x}=1+kt, \tag{1}$$

where x is the fraction of the materials transformed to the high pressure phase, which is supposed to be proportional to the change in resistance, *i.e.* since we can assume $R_L \gg R_H$,

$$1-x=\frac{R}{R_L}, \tag{2}$$

where R_L, R_H, and R are the resistances of the low-pressure phase and of the high-pressure phase, and the resistance at time t, respectively. From the values of the rate constant k obtained from Eq. (1) at various temperatures and pressures, the activation parameters for the transition in cadmium chalcogenides were calculated as listed in Table III (activation energy E_a, activation entropy $\Delta S^{\ddagger}$, and activation volume $\Delta V^{\ddagger}$). Those of other several substances are also included for the sake of comparison.

The decrease in the apparent activation energy E_a with pressure indicates that the mechanism is non-diffusional. In general, the activation energy for diffusion process is either increased with pressure for vacancy diffusion or relatively unaltered for interstitial diffusion, which will be referred later. In addition, the values of the activation energy for

Table III Activation Parameters of the Transitions

Substance	Pressure (kb)	E_a (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	Temperature (°C)	$\Delta V^{\ddagger}$ (cc/mol)	Reference
CdS	19.0	42	−11	100	−26	44
	22.3	14	−34	200	−36	
	13.7†	11†				
CdSe	20.7	32	−15	200	−24	
	23.8	12	−38	300	−31	
CdTe	28.3	9	−64	200	−35	
	31.9	5	−54	300	−38	
PbO_2		3.5				45
GeO_2	15.7～25.5	29±9			−15～−25	46
InSb I→II		100				43
InSb II→I		50				
P(red→black)	20	40.1	−16.0	179	−13.8	47
	60	23.4	−20.1	433	−15.2	
HgTe					−126	48
Yb					−17～−31	49

† Reverse transition

diffusion of cadmium or chalcogens in cadmium chalcogenides at or near atmospheric pressure* are even larger than those appeared in Table III. Therefore, we assumed these transitions as a diffusionless growth process.

Equation (1) is interpreted as a special case of Avrami's treatment[53] and formulated by Hornig *et al.*[54] as the following expression:

$$\frac{1}{1-x}=1+\sigma G N_g t, \tag{3}$$

where σ is the shape factor, G is the linear growth rate of a new phase, and N_g is the initial density of germ nuclei. The rate constant k is given by $\sigma G N_g$. Since σ and N_g are effectively constant, the dependence of k on temperature originate from G. Thus, the observed E_a represents the activation energy for the rate of the growth of the new phase, or, in this case, the progressive movement of the interface.

The influence of the crystalline size on the rates of the transitions has been also investigated. As the result, the rates of the transition for CdS and CdSe with larger crystalline size become the higher, while those for CdTe with larger size become the lower.

The values of E_a for CdTe are considerably smaller than those for CdS and CdSe. The values of ΔS^* for CdTe are larger than those for CdS and CdSe. These differences in the activation parameters and in the effect of crystalline size may come from the difference in the structures of low-pressure phase, *i.e.* in CdS and CdSe, wurtzite-to-rock salt transition and in CdTe, zinc blende-to-rock salt transition.

KINETICS OF SOLID-STATE REACTIONS BETWEEN TWO KINDS OF ELEMENTS; Zn-P AND Zn-As

It is not easy to find suitable reactions and experimental conditions for kinetic treatment, because further chemical changes are apt to take place which destroy the kinetic significance of the analysis. In the reactions between Zn and P, and between Zn and As, it was confirmed[12,13] that at the temperatures of 150–300°C and pressures up to 40 kb, only the following reactions took place in the solid-state;

$$3Zn+2P \longrightarrow Zn_3P_2 \tag{I}$$
$$3Zn+2As \longrightarrow Zn_3As_2 \tag{II}$$

The structure of Zn_3P_2 and Zn_3As_2 is tetragonal[55,56]. Figure 2 shows the melting curves of Zn, P, and As. The polymorphic transition line of red- to black- P is shown, too. We can find in chemical handbooks that red-P has the melting point of 589.5°C at 43.1 atm, but its pressure dependency is not clear. In our experimental conditions, however, all of the elements can be considered to be solid phase.

The facts that these reactions are retarded by increasing pressure after a relatively fast initial stage and that time *vs.* yield curves are parabolic suggest to the mechanism of these reactions a diffusion-controlled process. From the measurement of the Kirkendall effect by using Pt marker, diffusing species was confirmed to be Zn in both reactions.

Since Jander[60] published a model of the kinetics of diffusion controlled solid-state

* 46 kcal/mol for Cd in CdS,[50] 36–51 kcal/mol for Se in CdSe,[51] and 32–62 kcal/mol for Cd and Te in CdTe[52]

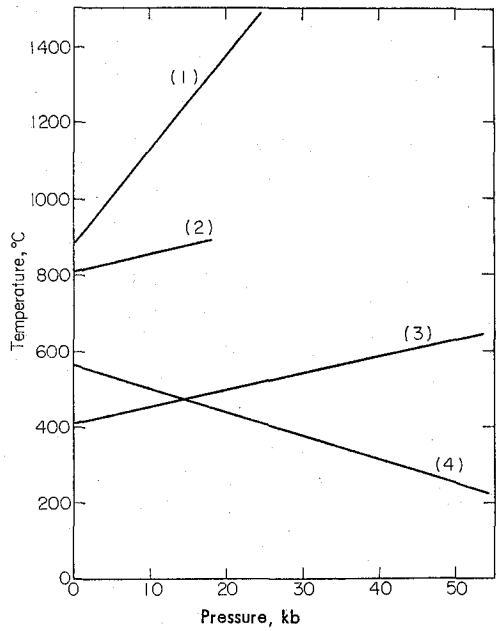

Fig. 2 Melting lines of (1): black-P[57], (2): As[59], (3): Zn[58], (4): polymorphic transition line of red- to black- P[47].

reactions in 1927, a number of workers have analyzed their data in terms of this model and some of them have revised this model. There are two oversimplifications in the analysis of Jander to be applied to the reactions of spherically shaped particles even if one of the two components is larger enough than the other. First, the reaction interface was assumed to be plane. Obviously, the rate of thickening of a spherical shell of the reaction product must depend upon the ratio of the areas of the outer to inner surfaces. The second assumption was made in equating the volume of sphere consisting of the unreacted part and the reaction product to the initial volume of one component. Therefore, this analysis would be expected to hold for small values of x. Based upon the equation used by Dünwald and Wagner[61] for gas-solid reactions, Serin and Ellickson[62] published a more rigorous diffusion-controlled rate equation for solid-solid reactions.

$$1-x=\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2kt), \tag{4}$$

where x is the fraction of the reaction completed at time t. The rate constant k is equal to π^2D/a^2. D is the diffusion coefficient based on Fick's law and a is the radius of the particles. In using this equation, x is determined by chemical analysis and the corresponding value of kt is obtained from a table.[63] Then kt is plotted against time. The resulting line should be straight if the process is diffusion-controlled and the assumptions of derivation are satisfied. However, straight lines have been obtained, even though the particles are not always spherical and the diffusion law is not entirely applicable.[64] Thus, Eq. (4) might be used as an empirical equation for powders.

All the curves representing kt *vs.* time give straight lines after the initial part of the reaction. The initial part of the reaction is also very nearly a straight line which passes

through the origin. This behavior is seemed quite general for the present reactions. Similar aspects have been observed for the solid-solid reactions between silver sulfate and cadmium oxide or strontium oxide.[64] The initial stage contains the grain boundary process, which is fast enough to be completed in a short time. Since the initial process is not purely diffusion-controlled, second-order rate equation was applied in the case of the reaction between Zn and As. After the surface reaction is completed and the surface is covered with product, the dominant factor controlling the reaction is the diffusion into grains, so-called volume diffusion. Calculating the volume differences ΔV between products and reactants in both reactions, we can obtain 1.18 cm^3/mol in Zn-P and 8.17 cm^3/mol in Zn-As. That is to say, the molar volume of the products is larger than the sum of the volumes of the reactants. With proceeding reactions, grain boundary becomes denser and it becomes favorable for the volume diffusion through the product layer. Table IV lists the activation energies E_a and activation volumes ΔV^* in both reactions.

The values of the activation parameters for self-diffusion may serve as a base of comparison with the present diffusion-controlled process. The data of Zn cited from the reference[65] are given in Table V. As for the diffusion of P, it is known little. Diffusion coefficient of P into Si is reported to be 10^{-12}–10^{-13} cm^2/sec even at 1200°C.[66] The values of the activation energy E_a for the present reactions in Table IV as well as those of activation enthalpy ΔH^* for the self-diffusion of Zn in Table V increase with increasing pressure. This is one of the characteristics of the diffusion-controlled process. The values of E_a are somewhat small as compared with ΔH^*. The stress in the crystal lattice of products caused by the volume increase ($\Delta V>0$) with proceeding reactions and by the non-hydrostaticity which is unavoidable more or less in the compression with solid medium tends to ease the formation of vacancies and consequently decreases the energy of activation. The remarkable appearence of the Kirkendall effect in the present systems substantiates the existence of vacancy in high concentration. The activation volume for diffusion may be considered as the combination of the volume change associated with the formation of vacancy $\Delta V_f^*$and the volume change associated with the movement of the atoms ΔV_m^*. In vacancy mechanism both values are positive. If there are many vacancies which are not produced by thermal process, only the contribution from ΔV_m^* will be enough to be considered. Presumably, this is why in Zn-As system, ΔV^* is small as compared with ΔV^* of the self-diffusion in Zn. The difference in the values of the activation volume between the systems Zn-P and Zn-As may be due to the difference

Table IV Apparent Activation Energies E_a and Activation Volumes ΔV^*

Pressure (kb)	Activation energy, E_a (kcal/mol)		Temperature (°C)	Activation volume, ΔV^* (cm^3/mol)	
	Initial process	Volume diffusion		Initial process	Volume diffusion
$3Zn+2P\rightarrow Zn_3P_2$					
5	13.0	14.2	200	2.6	3.3
10	13.3	14.9	250	3.6	4.1
$3Zn+2As\rightarrow Zn_3As_2$					
20	12.3	9.1	150	−0.5	1.4
30	11.8	10.6	200	−0.4	0.8
40	10.3	11.7	250	−0.3	0.7

Table V Activation Parameters for the Self-Diffusion of Zn^{65})

	Diffusion coefficient, D (cm^2/sec) at 307°C	
	1 atm	10000 atm
$D_{\parallel}$	8.33×10^{-10}	1.92×10^{-10}
$D_{\perp}$	2.60×10^{-10}	1.53×10^{-10}
	D(Polycrystalline) $3.3-3.6\times10^{-11}$ at 243°C	
	Activation enthalpy, $\Delta H^{\ddagger}$ (kcal/g·atom)	
	1 atm	8000 atm
$\Delta H^{\ddagger}_{\parallel}$	19.6	25.0
$\Delta H^{\ddagger}_{\perp}$	25.9	32.0
	(22.7–23.8 at 240–410°C)[67]	
	Activation volume, $\Delta V^{\ddagger}$ (cm^3/g·atom) at 307°C	
	1 atm	10000 atm
$\Delta V^{\ddagger}_{\parallel}$	16.87	3.62
$\Delta V^{\ddagger}_{\perp}$	4.95	2.68

$\parallel$ and $\perp$ mean parallel and perpendicular to the C axis, respectively.

in the atomic radii or the difference in the interactions with Zn between P and As.

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